Analysis of Mercury in Deep-Sea Grenadier

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Abstract

Mercury concentrations were measured in white muscle tissue of six different species of deep-dwelling rattail. Fish were collected from a deep-sea Point Sur expedition 2009 in Monterey Bay Canyon at different depths ranging from 1000m to 3000 meters. Total mercury was analyzed using cold vapor atomic fluorescence spectrometry. Values ranged from 48.9 to 1650 ng/g (ppb), and were tested for correlation with depth. Statistical analysis resulted in a significant positive correlation. The study of this paper is unique to the macrourid family of fish, and reflects similar results seen in previous studies on different pelagic fish species from a variety of depth categories.

Introduction

Biogeochemical Properties

Mercury is a trace element distributed through oceanic systems and other environments from a variety of sources. It can originate from natural and anthropogenic sources and has shown an increase over that past decade. (Lindberg et al., 2007) Volcanic activity and weathering rocks, deposits, and atmospheric deposition as well as historic deposits are all potential entryways of global mercury cycling. An article by Kraepiel et al. (2003) indicates three potential regions of entry for mercury in marine ecosystems: coastal sediments as well as slope sediments, low oxygen waters below productive ocean waters, and deep ocean sediments. Because of its toxic effects, mercury is commonly known as a global pollutant, and studies on the accumulation of mercury in living organisms, especially food sources has remained a lasting concern in both the scientific and medical community (Heppell, 2007).

Entry Points of Hg in Ecosystems

Basal trophic levels like bacteria are seen as main entry points into marine food chains. Evidence shows that mercury can be methylated by sulfate-reacting bacteria making ocean depths and surfaces more likely to produce methylmercury (Benoit et al., 2003). Organic matter decreases from watersheds to open ocean, and sulfate concentrations tend to increase. These as well as organic carbon concentration in pore water, will all strongly influence Hg bioavailability to the methylating bacteria (Sunderland et al., 2006). However, the combined effect of these on methylation, and uptake by organisms is less understood. From this entry point, the methylated mercury can accumulate in tissues of proceeding consumers, eventually reaching apex predators and entering human populations. MeHg concentrations and trophic levels have been shown by several studies to be positively correlated by using stable isotopes as markers (Bank et al., 2007; Driscoll et al., 2007; Hammerschmidt and Fitzgerald 2006).

Ecotoxicology and Toxicity

The ecotoxicology of mercury is worth noting since it can have adverse effects in fish, birds and mammals. It has been shown that 95% of mercury in tissues of organisms is generally methylmercury (MeHg), the more toxic species of mercury (Bloom 1992). MeHg groups are positively charged and are attracted to the nucleic acid cysteine. Biochemical studies of this complex have demonstrated its ability to be transported through the blood-brain barrier and cause neural damage (Kerpert, et all 1992). This becomes especially important in pregnant women because risk of mercury poisoning and subsequent brain injury is higher in fetuses, and can lead to developmental disorders.

Hg Bio-magnification and Bio-accumulation

More specifically, mercury has been shown to biomagnify as the depth of the ocean increases (Monteiro et al., 1996). In the study performed by Monteiro et al., the elevated mercury concentrations in fish below sub-thermocline low oxygen waters was directly attributed to food source of fish, and ultimately attributed to water chemistry controlling speciation and uptake of mercury into the base of the food chain (phytoplankton). During partitioning in phytoplankton cells, MeHg will mostly reside in the cytoplasm leading to better assimilation of this compound than its inorganic counterpart which tends to reside on the cell membrane of this unicellular organism. Furthermore there is a higher efficiency of MeHg uptake from ingested food than from water passed through gills (Phillips & Bulher, 1978). This further implies that trophic level and mercury concentration are related in the fish studied, and mercury is able to bio-accumulate in aquatic food chains.

The diverse studies focus on different environments and factors that affect mercury concentrations in food chains and individual organisms. However, the mercury cycling and uptake into biota via methylation vary in the source of study: coastal and slope sediments, low-oxygen waters below productive ocean waters, and deep ocean sediments (Chen et al. 2008). This means that the entry points of Hg into food chains will vary among regions and types of environments. The biogeochemical cycling factors that may be influencing this MeHg uptake can thus vary.

Hg Concentration in Fish

Factors influencing mercury concentration can also include age, size, life history (reproductive and developmental patterns) of specific fish species, as well as depth of habitat of deep-sea fish (Julshamn et al., 2011; Monteiro et al., 1996; Choy et al., 2009). For benthic fish species, experiments involving examination of stomach contents found that squid and shrimp were the most common prey items of ground fishes such as the giant grenadier (*Albatrossia pectoralis)* and the Pacific cod (*Gadus macrocephalus*)in the Gulf of Alaska (Yang et al., 2006). However, these studies also found prey items to include mysids, euphausiids, octopuses, walleye pollock, deep-sea smelts, and scorpaenids. Grenadiers are commonly known to be generalists, but studies on grenadier are scarce.

Rattail fish, commercially known as grenadier, are one of the most abundant families of fish in benthopelagic habitats throughout the oceans. More than 300 species of grenadier are considered benthopelagic (Geistdoerfer 1975). Formally referred to as Macrouridae, this gladiform family is closely related to the better-known cod. Grenadier are becoming increasingly relevant scientifically and commercially because they are often bycatch, and because their ubiquity in ocean regions can be a sign of importance within ecosystems, according to institutions like NOAA, NMFS (National Marine Fisheries Service), and locally based organizations like the North Pacific Fishery management Council responsible for setting management plans based on relevance and importance of certain fish species.

Additionally, grenadier could potentially become a large consumer product following the trends of consumption and exploitation of the blue-eyed grenadier also known as hoki (*Macruronus novaezelandiae*). In New Zealand the fishing and consumption of this fish increased with depletion of the long-lived deep-sea orange-roughy (Broad, 2009). Because deep-sea fishing has increased with the reduction and depletion of coastal fish communities, and deep-sea fishing technology has advanced into flash freezing, global positioning, and larger ship sizes, there is more concern involving deep-sea fish like the grenadier which have slow metabolisms and subsequent slow growth (Brown 2007). This slow growth could not only have an affect on the responsiveness of rattail populations to overfishing, but can also contribute to the concentrations of mercury in the tissue of these fish.

According to Monterey Bay Aquarium, grenadier are caught as bycatch, and the Giant Grenadier (*Albatrossia pectoralis)* is the most abundant and commonly caught accidentally while trawling for other fish like the Dover sole (MBAF, 2012; Clausen and Rodgveller, 2010). For this reason, and their particularly long life span, grenadiers are a species that MBA designates as a food choice to avoid in their Seafood Watch Guide (Monterey Bay Aquarium, 2012).

This study seeks a relationship between mercury concentration and depth in deep-sea grenadier. Mercury concentration in white muscle tissues of grenadier is predicted to increase with increase in depth. It will also comprehensively consider what is known about the diet of deep demersal fish to consider its effects on mercury concentrations, and consider other factors that might influence mercury levels as well. In the study performed by Choy et al. (2011), increasing mercury concentrations in certain prey species of fish, and their prey were attributed to depth of occurrence. This was concluded by considering the ecology of the specimen by stomach content analysis, and it was found that deep-dwelling prey contributed more to the mercury content of the predator fish tested. Compared to results from Monteiro et al. (1996), Choy et al. (2011) approached similar conclusions that diet and ecology are the proximate result of mercury load on fish tested. Depth in that study was thus a signifier of differences in foraging behavior and therefore contributed to differences in mercury concentration.

Methods

Fish were collected at Monterey Bay canyon (approximately 37ºN, 122ºW) using an otter trawl sent to 1000, 2000, 1300, and 3000 meters below sea level on top of the Point Sur ship (2009). Fish were dissected, and white muscle tissue was stored by deep freeze. Approximately 0.2-0.5g samples of white muscle were prepared and stored in small sample tubes, and mailed to the University of Idaho Analytical Sciences Laboratory in dry ice (February, 2012).

Mercury analysis was performed at the University of Idaho Analytical Sciences Laboratory with CVAFS (cold vapor atomic florescence spectrometry) using a Leeman HYDRA AF Automated Mercury Analyzer. Tissues samples were stored frozen in small sample tubes, and then weighed based on wet weight basis. The samples were digested for three days in 75mL digestion tubes with trace metal grade nitric acid (3%) and hydrochloric acid (11%) and homogenized samples were brought to volume. After digestion samples were diluted twice to prevent overshooting the instrumentation and data was consequently corrected for mercury concentration. Samples were centrifuged for 10 minutes at high speed in smaller 10mL tubes, and were then ready to be analyzed using the instrument.

During the process, mercury in sample is reduced to elemental mercury and argon is then used to remove mercury vapor from the aqueous phase in a gas-liquid separation chamber, and then quantified by cold vapor atomic fluorescence (ASLSM, 2011). The machine was warmed up by running the reagents through it for approximately 2 hours, and then was calibrated one replicate at a time to prevent drifting during sample analysis. One sample (*C. leptolepis* 2 at 3000 meters) resulted in foaming and over-flow during acid digestion and homogenization, and was thus excluded from the reported values.

Mercury concentration was calculated on the HYDRA AF by using volume of solution and weight information in the rack editor (ASLSM, 2011). Quality Control was assured using reagent blanks, a check standard, reference material (e.g. NIST, TORT-2), and a duplicate for additional certainty. Sample masses in this analysis were too small to provide duplicates, but all other quality assurance parameters were met, and quality control was approved by the laboratory director. The reporting limit using the standardized methods for this analysis is 8 ng/g (8 ppm). Depth and the ratio of THg/weight were then used to test for correlation between depth and THg level using SPSS.

Results

Total Hg concentration (THg) was determined with a range of 48.9-1650 ng/g or ppb (Table 1). The highest value was found to be on *C. acrolepis*7 with a THg of 1650 ng/g (ppb). The smallest value of 48.9 ng/g was found on *A. pectoralis* 1. The four largest fish were found to have the highest mercury concentrations (*C. acrolepis* 7 at 2195g, *C. filifer* 3 at 110g, *C. acrolepis* 1 at 1802 g, and *C. acrolepis* R1 at 1267g) with THg concentrations of 1650 ng/g, 1350 ng/g, 803 ng/g, and 668ng/g respectively. Mean THg/Weight for *C. acrolepis* was 0.52 ±0.138, 0.668 ±.296 for *C. armatus*, 1.516 ±0.609 for *C. leptolepis*, and 1.093 ±0.178 for *C. filifer*.

There was a significant positive correlation (Figure 1) between depth and THg/weight [$r=0.782$, $n=15$, $p=0.001$]. Strong correlation was also found between THg/weight and depth for species *C. acrolepis* [$r=0.999$, $n=3$, $p<0.05$] and *C. armatus* [$r=1$, $n=2$, $p<0.05$].

Table 1. Fish weight, depth of capture, total mercury concentration (ng/g) and the ratio between THg and body weight.

Fish Species, specimen number	Fish Weight (g)	Depth(m)	THg (ng/g)*	THg/Fish weight (ng/g^2)
A. pectoralis 1	793	1000	48.9	0.061664565
C. acrolepis; 1	1802	1000	803	0.445615982
C. acrolepis; 2	743	1000	375	0.504710633
C. acrolepis; 3	268	1000	105	0.391791045
C. acrolepis; R1	1267	1300	668	0.527229676
C acrolepis; 7	2195	2000	1650	0.751708428
C. armatus; 1	723	2000	249	0.34439834
C. armatus; 6	159	3000	117	0.735849057
C armatus; 5	681	3000	630	0.925110132
C. leptolepis; 1	56.5	3000	110	1.946902655
C. leptolepis; 3	258	3000	280	1.085271318
C. filifer; 3	1103	3000	1350	1.223934723
C filifer; 8	542	3000	631	1.164206642
C. filifer; 5	621	3000	553	0.890499195
C. yaquinae; 1	189	3000	238	1.259259259

Figure 1. Ratio of THg/fish weight of fish tissue samples plotted against depth ranging from 1000 meters to 3000 meters.

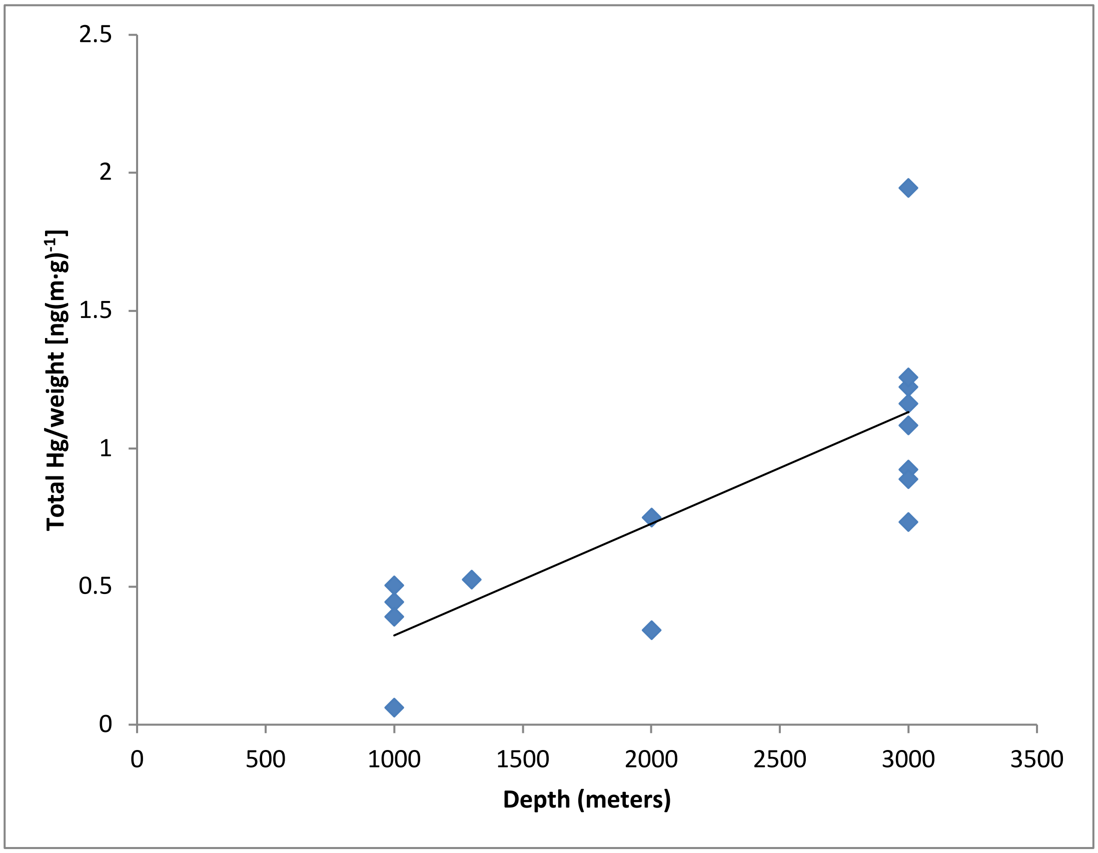
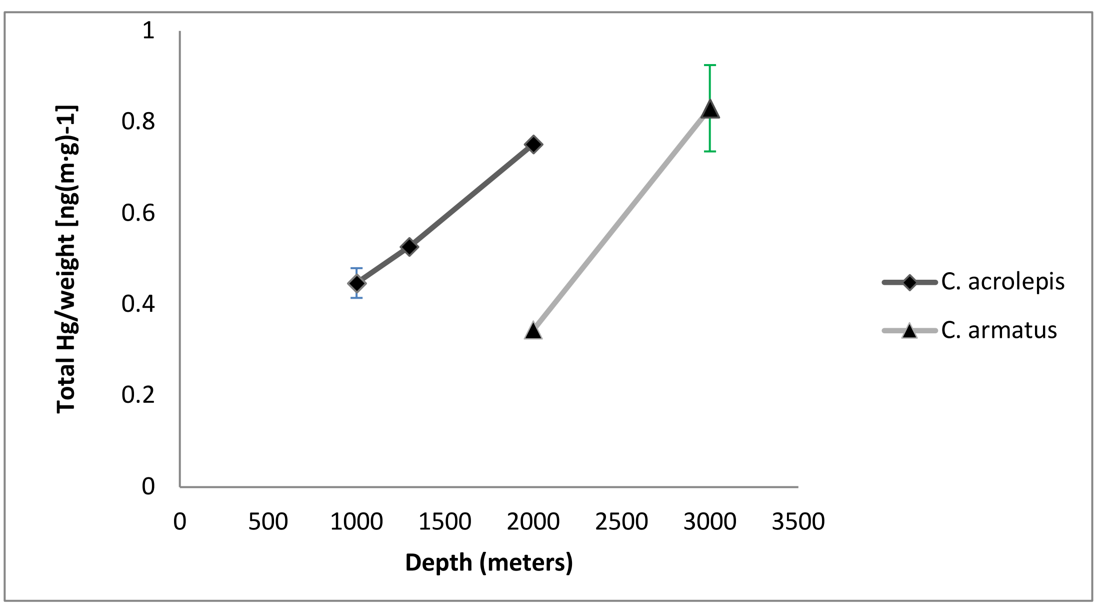


Figure 2. Ratio of Hg/weight of same species plotted against different depths ranging from 1000 to 3000 meters.



Discussion

The positive relationship found in statistical analysis is also demonstrated by the trendline in Figure 1. This is comparable to previous studies similar to this performed on deep-sea fish. Monteiro et al. (1996) found a significant positive correlation between mean Hg concentration in eight different species in the Azores (r_s=0.88, t_6=4.56, p<0.005). The results from Choy et al. 2009 who also analyzed mercury concentrations in several species at different depths in central North Pacific Ocean found a significant positive correlation (Log Thg=0.0014+2.2217; P<0.05, r^2=0.76). Aside from these two, there are no other studies analyzing mercury concentrations and depth in deep-sea fish. These three studies indicate positive correlation with increasing mercury levels and increasing depth. The pattern can be attributed to a variety of factors mentioned before, however..

Mercury concentration may be affected by species-specific physiological differences, and additional ecological differences like preferable depth or location among the structure of Monterey Bay Canyon. Diet, for example can affect the mercury concentration of these benthic fish. Little is known about individual species diet, but this study works under the knowledge that benthic grenadiers are generalists. Studies like Al-Reasi et al. on mercury content in fish have used stomach content analysis to analyze the diet of certain fish in order to characterize its behavior in aquatic food chains and gain a better understanding of the dynamics between ecology and concentration of toxic elements such as mercury (Al-Reasi et al., 2010).

Figure 2 reveals a positive relationship between depth and mercury levels regardless of species analyzed. Having ruled out possible species-specific factors affecting mercury concentration, it becomes more evident that depth is a determining factor in increasing mercury concentration in grenadier. Since this analysis was performed on white muscle tissue only, it runs under the assumption that these deep-dwelling fish have more or less the same generalist dietary pattern.

A summary article by Chen et al. (2008) discusses the behavior of mercury in aquatic ecosystems and its effects on humans. Highlighted in this article, is the need to develop methods and measurements that apply to wide set of ranges and biogeochemical conditions. There is a need to gather more data that analyzes the effects of various factors on mercury concentration in deep-sea fish, and consolidate that with what we already know about coastal and shallow populations of fish. Further experiments would need to focus on both species-specific diet, and an analysis of mercury bioavailability in Monterey Canyon.

An increase in market demand for deeper fish and improvements in deep fishing technology attract concerns for public safety, health, and conservation. Whether long-lived fish like the grenadier provide more benefits than not, will ultimately depend on the nature of these species and the factors that must be considered for public health. Mercury will always remain a major concern in the public and scientific communities because of the multitude of factors that can influence its entry and mobilization in ecological systems.

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